Non-Traditional Explosives: Potential Detection Problems

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Most explosive detection technologies have been focused on nitro-based military explosives because, indeed, they have figured in international terrorist incidents Not only are they readily available through purchase or theft or from sponsoring states, but methods for home synthesis of TNT, PETN and RDX are widely available. Presently substantial resources are being committed to developing explosive detection technologies to protect commercial aircraft, trains, tunnels, nuclear powerplants, etc. against such terrorist threats. Most of the systems now under development target a specific characteristic of military or commercial explosives (e.g., mass density, nitrogen density). However, as counter-terrorist measures make traditional explosives more difficult to obtain or more risky to use, we should anticipate terrorists may turn to non-traditional explosives. There are hundreds of energetic compounds and many common explosives which, while they do not meet exacting military demands, would be effective terrorist tools.

Although explosive handbooks list hundreds of explosives, the following discussion focuses on only a handful. These have been chosen because they meet the following criteria.

> They are explosives or pyrotechnics that do not follow the classic patterns of military explosives, which new detection technologies are expected to target.
>
> The selected energetic compounds are easily obtainable or are readily prepared.

This paper will also point out energetic systems that can produce violently exothermic reactions without the aid of traditional initiating systems, such as batteries or detonators.

Terrorist attacks generally fall into three broad categories: assassination; seizure (e.g., highjacking); and explosive destruction of a major asset, usually accompanied by substantial loss of life. The 1990s Mafia-linked assassinations in Sicily indicate the difficulties of protecting more-or-less private individuals against well-equipped and determined terrorists; this is unlikely to change in the foreseeable future. Seizures or

highjackings of embassies, commercial aircraft, cruise ships, etc. have and should continue to decline if existing and emerging countermeasures are implemented in conjunction with sound physical security practices. (In fact, the increase in attempts to destroy commercial aircraft during the past few years may be due to the improvements in anti-seizure technologies and practices.)

Explosive destruction can be accomplished externally or internally. Examples of external attacks include the use of shoulder fired surface-to-air missiles or mines laid on or under railroad tracks. This threat will not be addressed. Examples of internal attacks include all manner of improvised explosive devices smuggled onto commercial aircraft, into government buildings, etc. This paper will focus on technological developments in the area of internal explosive destruction. This is the area in which the greatest research and development efforts have been focused in recent years. The US Federal Aviation Administration, a world leader in this area, has spent well over $100 million on explosive detection R&D during the past decade, and the pace has been increasing. Furthermore, this is the area in which terrorists may have the greatest opportunities for circumventing the emerging counter-terrorist technologies.

Background

An explosion is a rapid expansion of matter into much greater volume. The expansion is such that the energy is transferred almost completely into mass motion, and this is accompanied by loud noise and a great deal of heat. Explosive devices may be mechanical, chemical, or atomic. An explosive substance is one which reacts chemically to produce heat and gas and a rapid expansion of matter. A detonation is a very special type of explosion. It is a rapid chemical reaction, initiated by the heat accompanying a shock compression, which liberates sufficient energy, before any expansion occurs, to sustain the shock wave. The shock wave propagates into the unreacted material at supersonic speed, between 1500 and 900 m/s.

Typical military explosives are organic chemicals; usually they contain only four types of atoms: carbon (C), hydrogen (H), oxygen (O), and nitrogen (N). To achieve maximum volume change, gas information, and heat release, explosives are designed to be dense, to have high oxygen content, and to have positive heats of formation. In monomolecular, organic explosives, this means explosives usually contain NO_2 groups. Upon detonation, exothermic reactions occur which transform nitrogen atoms into nitrogen (N_2) gas, while the oxygen

atoms combine with the hydrogen and carbon atoms to form the gaseous products H_2O, CO, or CO_2. This is similar to what happens in combustion, but a detonation is different from burning in two ways. In combustion, there is an unlimited amount of oxidiser available. An explosive reacts so quickly that it must have its own source of oxygen near at hand, either in the same molecule, as with most military explosives (e.g., TNT), or in a neighbouring molecule, as in the intimate mixture of ammonium nitrate and fuel oil (ANFO).

$4\ C_7H_5N_3O_6\ (TNT) \rightarrow 7\ CO_2 + 6\ N_2 + 10\ H_2O + 21\ C$
$37\ NH_4NO_3 + CH_3(CH_2)_{10}CH_3 \rightarrow 12\ CO_2 + 37\ N_2 + 87\ H_2O$

'Oxygen Balance' is a method of quantifying how well an explosive provides its own oxidant. There are various ways of defining oxygen balance (OB). One can balance the oxygen so that every carbon has one oxygen (balanced for CO) or so that every carbon has two oxygen (balanced for CO_2).[1] One can also balance in terms of weight percent oxygen in the explosive (OB) or in terms of oxidant per 100 grams explosive (OB_{100}).[2]

The second way in which a detonation differs from a fast burn (deflagration) is the manner in which the performance is evaluated. The performance of a fuel is based on the amount of heat it releases; the performance of an explosive has some relation to the heat it releases, but there is more involved than that. Detonation is unique in the rapid rate at which energy is released. A high explosive creates a tremendous power density:

	W/cm^3
Burning acetylene	10^2
Deflagrating propellant	10^6
Detonating high explosive	10^{10}

The performance of an explosive cannot be expressed in a single characteristic. Performance is dependent on the detonation rate or velocity, the packing density, the gas liberated per unit weight, and the heat of explosion. Detonation velocity, itself, is dependent on packing density, charge diameter, degree of confinement, and particle size.

Both the terms brisance and strength are used in describing the performance of an explosive. When an explosive detonates there is a practically instantaneous pressure jump from the shock wave. The subsequent expansion of the detonation gases performs work, moves objects, but it is the pressure jump which shatters or fragments objects. Brisance (from French for shatter) is a description of the destructive fragmentation effect on a charge upon its immediate vicinity. Since shattering effect is dependent upon the suddenness of the pressure rise, it is most dependent upon detonation velocity. Brisance is the term of importance in military applications. Brisance is often evaluated from detonation velocity, but there are 'crusher' tests in which the compression of lead or copper blocks by the detonation of the test explosive is taken as a measure of brisance.[1] Strength is important in mining operations; it describes how much rock can be moved. The strength of an explosive is more related to the total gas yield and the heat of explosion. It is often quantified with the Trauzl lead block test, where ten grams of a test sample are placed in a $61cm^3$ hole in a lead block and initiated with a No.8 blasting cap. Performance is evaluated from the size of the cavity created in the lead block.[3]

Explosives are often classified by the stimuli to which they respond and the degree of response. Propellants or deflagrating or low explosives are combustible materials containing within themselves all oxygen needful for their combustion. Examples are black powder and smokeless powder (colloided nitrocellulose). Detonating or 'high' explosives are characterised by their high rate of reaction and high pressure. In TNT or nitroglycerin, both high explosives, the shock wave travels at a speed of 6000 m/sec, compared to gun powder, a low explosive, in which it travels at 100 m/s.

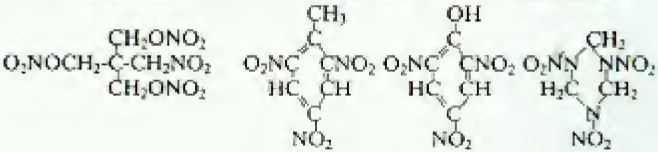
High explosives are subdivided into primary and secondary by the way they are initiated into the detonation, primary explosives are detonated by simple ignition-spark, flame, impact. They do not burn nor even necessarily contain the elements needed to burn. An explosion results whether they are confined or not. Examples of primary explosives are lead azide, lead picrate, lead styphnate, mercury fulminate, m-nitrophenyldiazonium perchlorate, tetracene, nitrogen sulphide (N_4S_4), copper acetylide, fulminating gold, nitrosoguanidine, potassium chlorate with red phosphorus (P_4), and the tartarate and oxalate salts of mercury and silver.

Secondary explosives require a detonator or primary explosive. Secondary explosives differ from primary explosives in not being initiated readily by impact or electrostatic discharge, and they do not easily undergo a deflagration-to-detonation transition (DDT). They can be initiated by large shocks; usually they are initiated by the shock created by a primary explosive. A fuze or blasting cap and frequently a booster are required. (A booster is a sensitive secondary explosive which reinforces the detonation wave from the detonator into the main charge). Like primary explosives, secondary explosives do not burn, nor do they require confinement. In general, they are more powerful, brisant, than primary explosives. Examples of secondary explosives include nitrocellulose, nitroglycerin, dynamite, TNT, picric acid, tetryl,

RDX, HMX, nitroguanidine, ammonium nitrate, ammonium perchlorate, liquid oxygen mixed with wood pulp, fuming nitric acid mixed with nitrobenzene, compressed acetylene and cyanogen.

Military explosives are secondary explosives, and they usually fall into one of three categories all of which contain nitro NO_2 groups. Nitrate esters, for example, nitroglycerin, nitrocellulose, PETN (active component in DETA sheet), contain $O\text{-}NO_2$ groups. These are possibly by oldest explosives still used by the military, nitration of alcohols having become a popular research topic in the 1830s and 1840s. Nitroglycerin and nitrocellulose became useful explosives by the 1860s. Nitrate esters are also the least stable military explosives; they lose NO_2 readily, making them relatively easy targets for vapour detection. Nitroarenes with a $C\text{-}NO_2$ linkage are typified by TNT (component of Composition B) or picric acid. Nitramines contain $N\text{-}NO_2$ groups; typical examples RDX and HMX are often the active components in plastic-bonded explosives such as Composition B, C-4, and Semtex.[4,5]

nitrate ester nitroarenes nitramine



	PETN	TNT	picric acid	RDX
Discovery	1894	1863	1742	1899
Used	1930	1900	1870	1940
g/cm^3	1.67	1.64	1.70	1.77
m/s	7975	6942	7480	8639
Cal/g	1510	1090	1270	1510

Discussion

Present explosive detection technology has focused on military explosives; and, indeed, they have figured in international terrorist incidents. Not only are they readily available for purchase or theft, but methods for home synthesis of TNT,[6] picric acid,[6,7,8] lead picrate,[7,8] PETN[9,10] and RDX[9] are widely available. However, there are hundreds of energetic compounds and many common explosives which, while they do not meet exacting military demands, would be effective terrorist tools. Therefore, as present day interdiction technology becomes more familiar to the public, we should anticipate terrorists may turn to non-military explosives.

Although explosive handbooks[1,2] list hundreds of explosives, the following discussion focuses on only a handful. These have been chosen because they meet at two of the following criteria. They must be explosives or pyrotechnics which do not follow the classic patterns of military explosives, which new detection technologies are expected to target. The selected energetic compounds are easily obtainable or are readily prepared. There is an attempt to point out energetic systems which can produce a violently exothermic reaction without the aid of a traditional initiating system.

Possible non-nitro-explosives can be identified by consulting the propellant, pyrotechnic, and fuel/air explosive literature. Many of these energetic materials can be classed as composite explosives, intimate mixtures of fuels and oxidisers. Peroxides are unique in that they can function as oxidisers in composite explosives or as stand-alone explosives, and triacetone triperoxide has reportedly been used in several terrorist incidents. Several self-igniting systems such as boranes, phosphorus, and alkali metals are discussed; for many of these, a blasting cap is not a requirement. In addition to non-nitrogen-containing energetic materials, several nitrogen-containing explosives in which nitrogen is not a part of the conventional nitro-group, will be discussed; included in this class is ammonium nitrate, the most available explosive worldwide.

Civilian Nitrogen-Containing Explosives

Nitromethane CH_3NO_2 is one of the few nitroalkanes which finds occasional applications as an explosive. It is a common industrial solvent and has a unique use as a fuel additive in hobby rockets and race cars. The explosive properties of nitromethane have been extensively studied since it is a relatively simple explosive (heat of explosion 1063cal/g; detonation velocity 6290m/s at density $1.138g/cm^3$; lead block test $400cm^3$). Although various propellant and explosive compositions have been patented, and for a time its use as a liquid monopropellant was considered, nitromethane has found no widespread military use. As a blasting agent, gelled nitromethane (gelled with guar gum or nitrocellulose) is comparable to ANFO (ammonium nitrate/fuel oil); it is more difficult to handle, but its higher density produces a high detonation velocity and energy output.[1]

The physical properties of nitromethane are such, a clear liquid with boiling point 101°C, melting point −17°C, and density 1.14g/cc (at 15°C),[1] that it could easily pass as water except for its unique odour (vapour pressure 37mm at 25°C). However, if nitromethane or a formulation

containing it, such as PLX, were bottled, with present detection technology, it would be very difficult to distinguish from water or wine. PLX (Picatinny Liquid Explosive), a slightly yellow liquid, contains 95 per cent nitromethane and 5 per cent ethylenediamine.[1] It was developed during World War II for mine-clearing operations. It was intended that the two ingredients be mixed just prior to use. PLX, in a whisky bottle, and 350g of Composition C4 in a radio were reportedly used in the downing of Korean Air Flight 858 (November 1987).

Ammonium Nitrate (AN, NH_4NO_3) is perhaps the most important raw material in the manufacture of industrial explosives (heat of explosion 627cal/g; detonation velocity 1000–3000m/s; lead block test 180cm^3). In 1986 over 11 billion pounds of ammonium nitrate were produced in the USA. Although its end use is mainly fertilizer, almost 20 per cent of it finds use in the explosive industry.[11,12] Ammonium nitrate has been used in explosive applications since 1867 when two Swedish chemists patented an explosive which used AN alone or mixed with charcoal, sawdust, napththalene, picric acid, nitroglycerin, or nitrobenzene. Nobel purchased the invention and used AN in dynamites. Amatol, developed during World War I, was a mixture of AN and TNT in various proportions: 50/50, 60/40, or 80/20. Amatols are not as brisant as TNT; the more AN, the less brisant and the lower the detonation velocity.[13]

Pure ammonium nitrate is considered an oxidiser rather than an explosive. AN was not considered an explosive until the 1921 disaster in Oppau, Germany, killing almost 600 people. In 1947 two different incidents occurred with ships loaded with fertilizer grade (wax-coated) ammonium nitrate (FEAN). In the first event at Texas City, Texas, the detonation of two shiploads of AN took about 600 lives; in the second in Brest, France, 20 died. When combustible non-explosives are added to ammonium nitrate, they react with the excess oxygen in AN to produce additional gas and heat, increasing the power and temperature of the explosion. The combustible non-explosive can be rosin, sulphur, charcoal, flour, sugar, oil, or paraffin, but most often it is a fuel oil. ANFO is a mixture of ammonium nitrate with 5–6 per cent fuel oil.

$$37\ NH_4NO_3 + CH_3(CH_2)_{10}CH_3 \rightarrow 12\ CO_2 + 37\ N_2 + 87\ H_2O$$

The preparation of ANFO can be as simple as pouring a fuel over a bag of ammonium nitrate. AN may be mixed more intimately with fuel in gels or emulsions. These materials came into use in the mining industry in the 1950s and 1960s, almost completely replacing dynamite. A typical ammonium nitrate aqueous emulsion contains 80 per cent AN, 14 per cent water, and 6 per cent fuel mixed with an emulsifier. Such a mixture can be easily whipped up in any kitchen.

The availability of ammonium nitrate is such that do-it-at-home explosives books[6,7] list many explosive formulations derived from it, and another such publication[14] labels ANFO as 'homemade C-4' and gives detailed instructions as to the proper grade of AN to purchase. Even AN mixed with aluminium is reported to be a powerful explosive.[8]

Ammonium Perchlorate is made by the electrochemical oxidation of sodium chloride NaCl to the chlorate $NaClO_3$ and on to the perchlorate $NaClO_4$. Like ammonium nitrate, ammonium perchlorate (of particle size greater than 45um) has been classed as an oxidizer rather than as an explosive for purposes of shipping (heat of explosion 4488cal/g; detonation velocity 3400m/s; lead block test 195cm^3). If the Texas City disaster of 1947 emphasised the explosive capacity of AN, then the PEPCON detonation of 1988, where half the US AP production capacity was lost and two people were killed, demonstrated the explosive power of AP. Both the French and Germans used ammonium perchlorate explosives during World War I.[13] The TNT equivalence of AP is about 0.31.

Mercury Fulminate $Hg(ONC)_2$ is a primary explosive, sensitive to heat, friction, and light (heat of explosion 355cal/g, detonation velocity 3500m/s at density 2g/cm^3). It undergoes marked decomposition above 50°C and is usually stored under water. Until the development of lead azide, mercury fulminate was practically the only explosive used in primers, basting caps and detonators, either by itself or in composition. Now it has largely been replaced by lead azide or diazodinitrophenol. Used in combination with fuels such as antimony sulphide (Sb_2S_3), mercury fulminate merely deflagrates, but in the presence of $KClO_4$, it can be used to ignite propellants. The synthesis of mercury fulminate is that the synthesis is included in several do-it-at-home explosives books.[6,8,10] Mercury is dissolved in concentrated nitric acid, ethanol is added, and the white crystals of mercury fulminate formed are thoroughly washed.

Azides are roughly divided into three classes: stable ionic azides (alkali and alkaline earth azides); unstable covalent azides (haloazides) which frequently explode spontaneously; and heavy-metal azides [$Pb(N_3)_2$, AgN_3] that explode with shock. It is the latter group which is often used as primers for initiating high explosives. The usual synthetic route is reaction of the metal nitrate with sodium azide.[15]

$$Pb(NO_3)_2 + 2\ NaN_3 \rightarrow Pb(N_3)_2 + 2\ NaNO_3$$

The synthesis of sodium azide has been published so that the terrorist can prepare it and, hence, lead azide, in his kitchen.[7] However, sodium azide itself will soon be widely available as it is used in most automobile air bags; and in many passenger-side air bags up to a half pound is used. Lead azide has respectable explosive properties (heat of explosion 367cal/g; detonation velocity 5300m/s at density 4.6g/cm^3; lead block test 110cm^3).

Nitrogen Triiodide NI_3, due to its low brisance and high sensitivity, has no practical use in the energetic materials community.[1] However, it has remained a favourite of teenagers due to its ready synthesis. This is probably the reason its synthesis is also included in the do-it-at-home explosive literature.[6] Iodine crystals are added slowly to concentrated ammonium hydroxide. A brownish-red precipitate forms. The precipitate is filtered and washed with alcohol and ether. This material can be handled only when wet because when dry, the slightest touch, such as a fly, can set it off.

Urea Nitrate Urea nitrate is stable, does not deliquesce, and is a powerful, cool explosive (heat of explosion 796cal/g; detonation velocity 3400m/s at density $0.86 g/cm^3$; lead block test $270 cm^3$). Its disadvantage for military use is that it is corrosively acidic in the presence of moisture.

$$(NH_2)_2{-}C{=}O + HNO_3 \rightarrow (NH_2)_2{-}C{=}O\ HNO_3$$

Although this material may be easily detectable, it is included in this listing of terrorist opportunities because it is often cited in the do-it-at-home literature and because the cited starting materials nitric acid and urine are easily obtained.[8] This is probably a good illustration that nitration, practiced on a variety of materials, yields an explosive—sugar, cotton clothing, aluminium foil.

Urea nitrate can be made more powerful by adding aluminium or by drastic dehydration.[1,8] Nitrourea, prepared by dehydration of urea nitrate with concentrated sulphuric acid, is a much more powerful explosive, a nitramine, in fact (heat of explosion 923cal/g).[10] Nitrourea decomposes in the presence of moisture.

Nitrogen-Free Explosives

Some potential non-nitrogenous explosives can be identified by consulting the propellant, pyrotechnic, and fuel/air-explosive literature. The boundary between such energetic mixtures is often vague, since the terms propellant, pyrotechnic, and explosive tend to be used to describe end uses rather than chemical composition. A propellant and an explosive can have the same active ingredient. Most of potential non-nitrogenous explosives can be broadly classed as composite explosives. Rather than containing the oxidiser and fuel in a single molecule, as do the organic military explosives, composite explosives are formed by intimately mixing oxidising compound(s) with fuel(s). These can be pre-mixed or mixed just prior to use. In such mixtures there can be problems due to inhomogeneities; the finer the solid particle size and the more intimate the mix, the better the performance.

A classic example of a composite explosive is black powder, a mixture of the oxidizers KNO_3 and sulphur with the fuel charcoal. As with black powder, the performance of many of these mixtures is related to the degree of confinement. ANFO, a mixture of ammonium nitrate and fuel oil, is another good example of a composite explosive. While military explosives have been common in international terrorism, in domestic terrorism in the US black powder, smokeless powder (nitrocellulose based) and flash powder (KNO_3, $KClO_4$, sulphur) have been the three most common explosive fillers.[17]

Tables 1 and 2 below list oxidisers and fuels which can be combined to form composite explosives. Most contain no nitrogen and are either commercially available or easily prepared.[18]

TABLE 1

OXIDISERS

oxygen and halogens	
perchlorates	$KClO_4$ & NH_4, Na, Ba, Ca salts
chlorates	$KClO_3$ & Li, Na, Ba salts
hypochlorite	$Ca(OCl)_2$
nitrates	KNO_3 & NH_4, Na, Ba, Ag, Sr salts
chromates	$PbCrO_4$ & Ba, Ca, K salts
dichromates	$K_2Cr_2O_7$ & $NH_4Cr_2O_7$
iodates	KIO_3 & Pb, Ag salts
permanganate	$KMnO_4$
metal oxides	BaO_2, Cu_2O, CuO, Fe_2O_3, Fe_3O_4, PbO_2, Pb_3O_4, PbO, MnO_2, ZnO
peroxides	Na_2O_2, H_2O_2 (80%), dibenzoylperoxide

TABLE 2

FUELS

nitrobenzene	petroleum	halogenated hydrocarbons
nitrotuluenes	turpentine	halogens
nitronaphthalene	naphtha	powdered metals
nitrocellulose	castor oil	carbon disulphide (CS_2)
picric acid	sugar	phosphorus (P_4)
	glycerin	sulphur (S_8)
	acetylene	
	wax, paraffin	
	sawdust	

Liquid Oxidisers In 1895 liquid oxygen explosives (LOX) were invented by Linde, who had developed a successful machine for the liquefaction

of gases. LOX are formed by impregnating porous combustible materials with liquid oxygen. Lampblack is the absorbent combustible most commonly used. The detonation velocity of the C/O_2 mixture averages 3000m/s.[19] Two problems exist with liquid oxygen containing explosives: they lose their explosiveness as the liquid oxygen evaporates (boiling point −183°C); and they are easily inflamed. During World War I the Germans use LOX when other explosives ran low. In 1926 LOX were used for the first time in commercial rock blasting operations; their use was continued into the 1960s.

Acetylene is usually thought of as a highly flammable gas, but it is also detonable as a gas, as a liquid (boiling point −80°C), or as a solid (melting/freezing point −84°C), acetylene is an explosive. The detonation velocity of solid acetylene is 2270m/s; combined with liquid oxygen (acetylene 25% /O_2 75%) the detonation velocity is comparable to high explosives (6000m/s).[1]

$$H-C\equiv C-H + \text{liq } O_2 \rightarrow 2\ CO_2 + H_2O$$

Below 21°C nitrogen dioxide (NO_2), a toxic gas, condenses to a colourless liquid, nitrogen tetroxide (N_2O_4). Below −11°C it becomes solid.

$$2\ NO_2\ (g) \longleftrightarrow \text{am } N_2O_4\ (\text{liq})$$

Explosives made with liquid N_2O_4 and combustible liquids (carbon disulphide, nitrbenzene, nitrotoluene, gasoline, halogenated hydrocarbons) were first suggested in 1881 and were generally termed Panclastitics. The Germans tested marine torpedoes containing sealed glass container of N_2O_4 and CS_2 in the 1880s; set-back forces broke the glass containers generating the explosive mixture, and an impact fuze initiated detonation. In World War I, when other explosives were in short supply, the French used Anilites, where liquid N_2O_4 and a fuel were enclosed in separated compartments of a bomb; after the bomb was dropped, passage of air by the nose opened a valve permitting the two liquids to mix.[13] In World War II Panclastites were used in some of the heaviest British aircraft bombs.

Panclastites are inexpensive and easy to prepare; some are more brisant and have better detonation velocities than TNT or picric acid. However, though their performance is favourable, Panclastites are too shock sensitive, too hard to handle, to find common military use. Their extreme sensitivity dictates that they be mixed just prior to use, and the corrosive nature of N_2O_4 requires special vessels. The N_2O_4/fuel mixtures can be absorbed on Kieselguhr to form a soft non-plastic material, which has too high a freezing point for military use. A mixture of 35 parts of carbon disulphide/NB (35/65) with 65 parts N_2O_4 has a lead block test of 435cm^3. Mixtures of N_2O_4 with 64 per cent nitromethane

have a detonation velocity of 6900m/s. Nitrogen tetroxide explodes on contact with several fuels: acetic anhydride, liquid ammonia, methyl and ethyl nitrate, propene, hydrazine-type fuels.

Oxides of Chlorine Among the oxides of chlorine, perchlorate is the most stable, but all are energetic and produce toxic fumes. Only chloric and perchloric acids can be isolated. Their reactivity follows that of the salts. They violently react with combustible, chloric acid being the more reactive.

$$ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$$

hypochlorite chlorite chlorate perchlorate

In World War II the US used Galcit propellant that incorporated $KClO_4$ (75 per cent) into molten asphalt (25 per cent).[1,3] It was the precursor of modern composite propellants in which ammonium perchlorate is embedded in a polymer. $KClO_4$, mixed with MnO_2 and a fuel, ignites spontaneously.

Among the oxidizers, chlorates ClO_3^-, are especially hazardous to handle. They decompose exothermically and are sensitive to heat, impact, and friction. Many chlorate mixtures, particularly those which contain sulphur, sulphide, or picric acid are extremely sensitive to blows and friction. The sensitivity can be reduced by phlegmatization in castor oil. Chlorate explosives with aromatic nitro compounds have higher detonation velocities and are more brisant than those in which the carbonaceous material is merely combustible. In 1885, 240,000lb of a mixture of $KClO_3$ (70 per cent) and nitrobenzene (21 per cent) along with 42,000lb dynamite were used to blast a portion of Hell Gate Channel in New York harbour. Other similar mixtures are turpentine/phenol (90/10) absorbed on $KClO_3/MnO_2$ (80/20) or nitrobenzene/turpentine (80/20) absorbed on $KClO_3/KMnO_4$ (70/30).

Mixtures of chlorate and fuel will spontaneously ignite with the addition of a drop of concentrated sulphuric acid (H_2SO_4). Spontaneous ignition or explosion can occur when alkali chlorates are combined with very reactive fuels (such as phosphorus, sulphur, powdered arsenic, or selenium) or with moist fuels. In fact, when powdered, dry, unoxidized $KClO_3$ and red phosphorus (Armstrong's powder) are pushed together, they ignite; this reaction has been tamed and utilised by use of separation and a binder in the common safety match. Armstrong's powder, wet with some volatile solvent such as methanol, has been used as an antipersonnel device. MnO_2 has been reported as a catalyst for the decomposition of chlorates. One do-it-at-home explosive book suggests an explosive filler of 9 parts $KClO_3$ and 1 part petroleum jelly or 3 parts $NaClO_3$ to 2 part aluminium or 3 parts $NaClO_3$ to 2 parts sugar.[8]

Calcium hypochlorite [$Ca(OCl)_2$] ignites spontaneously with glycerin.

Hypochlorites are generally highly reactive and unstable, but the calcium salt (HTH) is one of the more stable hypochlorites with the abbreviation HTH. Many forms of hypochlorite are available to the public: as liquid household bleach (an alkaline solution of $NaOCl$); as household dish washing detergents and scouring powders $[(Na_3PO_4 \cdot 11H_2O)_4 NaOCl]$; as a liquid bleach for pulp and paper bleaching [a mixture of $Ca(OCl)_2$ and $CaCl_2$]; and as a powdered swimming pool bleach [$Ca(OCl)_2/CaCl_2/Ca(OH)_2 \cdot 2H_2O$]. Discussing a mixture of 70 per cent HTH (from a swimming pool supply house) and petroleum naphtha (sold in hardware and paint stores) in a 30/1 ratio, one do-it-at-home book states, 'This mixture forms a low power/brisant high explosive which should be used under strong confinement and only as an explosive filler for antipersonnel fragmentation bombs.'[8]

Metals Some alkali metals spontaneously ignite on exposure to water or air. As the alkali metals increase in weight, their reaction to air becomes more violent. While potassium may oxidise so rapidly that it melts and ignites when pressure is applied (as in cutting), cesium burns in air as soon as it is removed from an inert oil covering. Moisture in the air serves to enhance further reactivity. Sodium and potassium form a eutectic (NaK) which is spontaneously ignitable. Sodium/potassium alloys are reported to react explosively upon contact with silver halides or to detonate upon contact with halogenated organic materials such as carbon tetrachloride. Potassium and heavier alkali metals burst into flame upon contact with water. Sodium too will inflame in water if it can be anchored in one spot long enough to allow the heat of reaction to ignite the hydrogen being produced:

$$Na + H_2O \rightarrow NaOH + 1/2\ H_2.$$

Lithium is the least reactive alkali metal but will ignite if thrown on water as a dispersion. In World War II the Germans used land mines composed of sodium and methyl nitrate in separate compartments. Pressure brought the two together and into action.

Some finely-divided (powdered) non-alkali metals will also burst into flame in the presence of air. The best known are lead, iron, nickel, cobalt, and aluminium. These can be prepared by pyrolysis of their organic salts or by reduction of their oxides, or in some cases, by formation of a mercury amalgam. These metals may also explosively react with water, halogenated hydrocarbons, and halogens. One do-it-at-home explosives book suggests the syrupy mixture of powdered aluminium and carbon tetrachloride as a cap sensitive explosive; the source of aluminium is the paint store.[8]

$$Al + CCl_4 \rightarrow AlCl_3$$

Magnesium is used in several pyrotechnics. When a magnesium/silver

nitrate mixture is moistened, it reacts explosively. Teflon $(C_2F_4)_n$ with powdered magnesium reacts explosively upon ignition. Devices of this composition are used as decoys for heat-seeking missiles.

$$(C_2F_4)_n + 2n\ Mg \rightarrow 2n\ C + 2n\ MgF_2$$

Some methyl- and ethyl-substituted metals are spontaneously ignitable in air. The alkylated metals most frequently exhibiting this behaviour are the alkali metals (Li, Na), aluminium, zinc, and arsenic or non-metals such as boron and phosphorus. Many of these compounds also react explosively with water and with carbon tetrachloride, (CCl_4). It is reported that triethylaluminum [$Al(C_2H_5)_3$] in carbon tetrachloride reacts explosively when warmed to room temperature.

Thermite is generally the redox reaction between a metal oxide and a metal. However, the most important reaction and the one usually referred to by this name is that of aluminium and iron oxide:

$$8\ Al + 3\ Fe_3O_4 \rightarrow 4\ Al_2O_3 + 9\ Fe$$

This reaction generates a tremendous amount of heat; molten iron is produced and its melting point is above 1530°C. One peaceful application of this reaction is for welding in shipyards and railroads. In fact one home-military manual[8] cites these as likely places to obtain pre-mixed thermite for incendiary devices. With $KMnO_4$ in the metal mixture, reaction can be triggered with added glycerol. With sugar in the initial mix, reaction is triggered with a drop of concentrated H_2SO_4. Thermite reactions using CuO or Mn_3O_4 are reported explosive. Mixtures of Pb, PbO_2, and PbO also undergo explosive thermite reactions.

Acetylides Some metal carbides exist which are explosive in their own right; most are termed acetylides rather than carbides. Copper acetylide and silver acetylide are most commonly prepared by teenagers. Being primary explosives, they explode violently upon heating, impact, or friction. Cuprous acetylide is the only acetylide which has been used in the explosives industry; it has been used in electric detonators. Acetylides can be formed by passing acetylene through a solution of the appropriate metal salt.

Peroxides Peroxides, with oxygen in the -I oxidation state, can be violent oxidizers in the presence of fuel. For example, sodium peroxide Na_2O_2 instantly ignites in the presence of moisture and a fuel (magnesium and sawdust or paper, or sulphur or aluminium). In addition to this feature, peroxides also can undergo a violent self-decomposition. Peroxide decomposition into water and oxygen can be catalysed by small amount of alkaline lead, silver or manganese salts or even saliva.[1,20]

Hydrogen peroxide may be a particularly appealing alternative to traditional explosives since bottled it can easily pass as mineral water. Pure

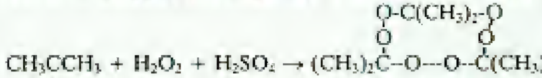
hydrogen peroxide decomposes violently above 80°C; therefore, it is sold as aqueous solutions (27.5, 35, 50, and 70 per cent in water). It is available at local pharmacies as a 3 per cent solution for use as disinfectant or as a 40 per cent solution for use as a hair lightener or as a gel to brighten teeth. It can also be concentrated in the laboratory. Pure hydrogen peroxide is readily detonable with a heat of explosion of 24.6kcal/mol. Hydrogen peroxide in concentrations as low as 86 per cent undergoes detonation above 50°C. Solutions of 90.7 per cent peroxide have reported detonation velocities of 5500 to 6000m/sec. Mixtures of hydrogen peroxide vapour is air with as little as 35mol% H_2O_2 are reported to detonate at 1 atmosphere with a velocity of 6700m/sec. Furthermore, hydrogen peroxide, pure or in water, is readily detonable when mixed with organic materials. H_2O_2/water/ethanol has a detonation velocity of 6700m/sec. The violence of the reaction is dependent upon the amount of water present, since water acts as an energy sink for the reaction.[1]

Austria made unsuccessful attempts to use H_2O_2 as an explosive in World War I. In World War II the US Navy used it for propulsion in submarine torpedoes. Peroxide explosives have been successfully used in blasting operations. In addition to its monergolic application, hydrogen peroxide can be mixed with fuels such as methanol, ethanol, or glycerol and show detonation rates as high as 6700m/s. One of the propellant systems on the space shuttle uses the combination of hydrogen peroxide and unsymmetrical dimethylhydrazine. H_2O_2 (60 per cent) with paraformaldehyde forms a crystalline compound of high brisance and sensitive (melting point 50°C). Hydrogen peroxide (70 per cent) with diesel fuel and gelling agent also makes a good explosive. H_2O_2 (83 per cent) plus cellulose forms a gelatinous mass which is more powerful than TNT and insensitive to shock or friction. It has an ignition temperature 200°C; however, it cannot be stored over 48 hours without evolution of peroxide and loss of explosive power. Other patented peroxide explosives include H_2O_2 with water and glycerol, H_2O_2 (70 per cent with powdered boron (30 per cent), and H_2O_2 used with hexamethylenetetramine and HCl.[1]

In general, alkyl peroxides tend to be more hazardous than inorganic peroxides. Many alkyl hydroperoxides (ROOH) are reported to explode violently on jarring. Dialkyl peroxides (ROOR) are apparently more shock sensitive. Diacyl peroxides have such notations as 'explodes without apparent reason'. Dibenzoyl peroxide $C_6H_5COO\text{-}OOCC_6H_5$ is one of the few commercially available alkyl peroxides predictable enough for terrorist use.

Two peroxides can be synthesized from acetone, a dimer and a

trimer. The dimer is more difficult to handle, but the trimer, triacetone triperoxide (TATP), is the suspected energetic in several terrorist incidents. The preparation of TATP described in the do-it-at-home explosive literature calls for mixing acetone and hair beach (15–25 per cent hydrogen peroxide) and adding of sulphuric acid (battery acid).[1,6] The white crystalline solid which forms after standing 24 hours explodes violently upon heating, impact, or friction. It is highly brisant, very sensitive, and detonable under water. Its reported detonation velocity is 5290m/s. It has been suggested for use in primers and detonators, but due to its volatility and sensitivity, it has not found military application.



Self-igniting materials Some chemicals are so reactive to the oxygen in air or to water that they spontaneously ignite. Three parameters affect the spontaneity of ignition in air: the dryness of the air, air pressure, and temperature. Most of these chemical systems cannot be classed as explosives, but if sufficient gas pressure and heat are evolved the effect could be catastrophic. A far more important hazard, however, is the use of such devices as wireless, metal-less initiators of a more powerful explosive device.

Hydrides Phosphines, silanes, and boranes ignite on contact with air. Diphosphine (P_2H_4) a liquid at room temperature, can be made from the reaction of water with solid calcium phosphide (Ca_3P_2), which, in turn, can be formed from lime and red phosphorus. Adding water to calcium phosphide results in a mixture of phosphine and diphosphine, and a violent deflagration ensues. This reaction has been exploited in naval flares.

Only mono- and di-silanes (SiH_4 and Si_2H_6) are stable to air at room temperature. The higher silanes decompose violently. Silane gas is available in large quantities for the manufacture of microelectronic components.

Diborane (B_2H_6) is a gas available in cylinders or by the action of 85 per cent phosphoric acid on $NaBH_4$. The gas is highly toxic, and, unless it is extremely pure, it reacts with oxygen at room temperature. Borane decomposition in oxygen is extremely exothermic; therefore, boranes, such as decaborane (14) ($B_{10}H_{14}$), have been seriously considered as a component in rocket fuel.

Phosphorus White phosphorus tends to ignite with slight pressure or by contact with fuel. P_4 self-ignites in air above 34°C; as a result, it is usually stored under water. The finely divided phosphorus left on the combustible material reacts exothermically with the oxygen in air:

$P_4 + 5\ O_2 \rightarrow P_4O_{10}$

The heat of this reaction initiates the reaction between carbon disulphide and air. Drying of the phosphorus can be delayed by addition of a high-boiling hydrocarbon such as gasoline or toluene. In contrast to white phosphorus, red phosphorus is nontoxic and less sensitive. Red phosphorus bursts into flames or explodes on mild friction or impact in mixture with chlorate, permanganates, lead dioxide (PbO_2), perchlorate, and other active oxidizers ($AgNO_3$).

Miscellaneous Energetics Potassium permanganate and glycerin will ignite spontaneously after a small delay, due to the difficulty in wetting the $KMnO_4$ with viscose glycerin. Ethylene glycol, acetaldehyde, benzaldehyde, or DMSO could be used in place of glycerin. Potassium permanganate and concentrated sulphuric acid can readily inflame when in contact with fuels. $KMnO_4$ was once a common medicine for farm animals:

$14\ KMnO_4 + 4\ C_3H_5(OH)_3 \rightarrow 7\ K_2CO_3 + 7\ Mn_2O_5 + 5\ CO_2 + 16\ H_2O$

Conclusions

Present advances in explosive detection technology have either focused on detection of conventional military explosives or on the presence of visually recognizable components. This is an entirely reasonable approach since we have every reason to believe that terrorists bent on destruction will continue to use such dependable, high performance devices until we find a way to stop them. The task of developing effective detectors for small improvised explosive devices has been arduous, and the objective has yet to be fully accomplished. Unfortunately, once we have put such detectors in place, we should prepare to deal with a new generation of devices based on non-military explosives. The range of explosives and the packaging possibilities is staggering. To this also should be added the incendiary devices, which might trigger a more powerful material or which, with proper placement, might prove to be every bit as devastating as an explosive. A 'bomb' no longer is a recognisable sphere or pipe, nor does it necessarily need a blasting cap or squib. Every bottle, can of hair spray or shaving cream, every vacuum bottle of coffee is a possible device.

This discussion has been limited to non-military and 'exotic' explosive devices. Ignored has been the threat of traditional military explosives, weaponry, biological warfare agents, chemical warfare agents, and fire. However, it should be noted that in most of the systems discussed herein, even if the outcome were not a detonation, a vigorous fire and/or toxic fumes would result. This discussion is intended to provoke new trains of thought on possible terrorist opportunities. While some of

the materials considered are thought to be too hazardous for everyday military use, terrorists may regard the level of risk as acceptable. More advanced explosive detection technology must be developed, and non-nitrogenous explosives should be targeted. Yet, now and in the foreseeable future, profiling, intelligence gathering and analysis, sound physical security practices, and common sense may remain our best security measures.

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